

Steam reforming of bio-oil from pyrolysis of MBM over particulate and monolith supported Ni/ γ -Al₂O₃ catalysts



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HIGHLIGHTS

- Bone oil was converted to environmentally friendly gas product rich in H₂ and CO.
- Catalytic steam reforming of bone oil was carried out using a dual catalytic system.
- The first reactor contained calcined granular dolomite as guard catalyst bed.
- The active Ni/ γ -Al₂O₃ catalyst was used in granular or monolith-supported form.
- The product gas can be used as fuel for gas engines or as syngas after purification.

ARTICLE INFO

Article history:

Received 13 June 2012

Received in revised form 17 April 2013

Accepted 1 May 2013

Available online 18 May 2013

Keywords:

MBM pyro-oil

Steam reforming

Dolomite

Ni/ γ -Al₂O₃ monolith

H₂-rich fuel gas

ABSTRACT

Catalytic steam reforming of bone oil, obtained by pyrolysis of meat and bone meal (MBM), was studied over particulate and monolithic Ni/ γ -Al₂O₃ catalysts and their promoted varieties. Two tube reactors were used in cascade at atmospheric pressure and steam to carbon molar ratio of 5. The first reactor, loaded with granular dolomite, and the second reactor, containing Ni/ γ -Al₂O₃ catalyst, was operated at 800 and 700–750 °C, respectively. The WHSV of the oil in the second reactor was usually in the range of 4.0–9.0 h^{−1}, whereas in the first reactor was generally ten times lower. The guard catalyst prevented the Ni-catalysts from activity loss for days and could be regenerated by air treatment at the reaction temperature. The oil was virtually fully converted to CO and H₂-rich gas. The K or Ca additives promoted, the Mg additive adversely affected the reforming activity and stability of the Ni/ γ -Al₂O₃ catalysts.

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1. Introduction

Due to the economical, political, and environmental concerns, associated with the use of fossil energy resources, there is growing need for technologies to convert nuclear or renewable energy to energy carrier liquid or gaseous fuel [1–3]. The abundantly available biomass is the primary renewable carbon source of fuel production [4–13]. Causing food price increase the use of renewable vegetable oil, sugar, and energy plants as fuel resource is less favored than the organic wastes and by-products. The fuel obtained from agricultural and forestry residues, and industrial wastes are referred to “second generation” biofuels [2]. Just like the first generation fuel production, the waste processing involves also thermochemical, chemical and biological conversion methods

[1,2]. The known technologies concern almost exclusively the conversion of biomass from plant origin.

At present the prevailing practices of thermochemical biomass conversion are the gasification at high temperature (800–1000 °C) in the presence of steam and/or oxygen, and the pyrolysis at moderate temperature (400–500 °C) [1,2,14]. The gasification results in CO and H₂ rich gas mixture that can be used as fuel to run engines and gas turbines, converting the chemical energy of the biomass to mechanical/electric energy. From CO/H₂ mixture more valuable energy carriers can be obtained, such as, hydrogen and liquid hydrocarbon fuel in catalytic water–gas shift (WGS) and Fisher–Tropsch (FT) reactions, respectively. The increasing oil and gas prices force the development and broader use of the FT technology and increases the demand for renewable CO/H₂ synthesis gas. The value of renewable H₂ is also increasing as the H₂-fuelled highly efficient energy converter polymer electrolyte membrane type fuel cells (PEMFCs) gain importance.

The raw gas, obtained from thermochemical biomass destruction contains tar, comprising of heavy polyaromatics that seriously

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hinder the application of the gas. The problem with the tar is that it can condense at different parts of any apparatus causing blockages and corrosion [14–16]. Gas cleaning and transformation of the clean gas to more valuable energy or energy carrier can be economical in large plants only. However, it is expensive to collect and transport the waste or the dirty raw gas to central processing facilities [2,5,11]. The rational control of the pyrolysis process offers solution for this problem. The fast pyrolysis produces mainly condensable organic liquid products (70–80%), the so called bio-oil, which can be collected, stored and transported more easily than the gas [2,6–11,13,17]. This advantage makes the fast pyrolysis process increasingly popular for biomass conversion. The bio-oil product has significantly higher energy density than the biomass used as pyrolysis feedstock. However, the utilization of bio-oils is limited because it is usually a polar, viscous, corrosive fluid that is immiscible with normal hydrocarbon fuels and prone to chemical deterioration during storage. Therefore, their use as conventional fuel or fuel additive without refining can be ruled out. The processes of transforming crude bio-oils to fuels or fuel additives are mostly catalytic and involve gasification by steam reforming, hydrotreating (heteroatom removal), cracking, decarboxylation/oligomerization and esterification [2,18].

The catalytic steam reforming of bio-oils gives CO and H₂-rich gas, which is similar to that obtained by direct biomass gasification. Due to their relatively low price and reasonably good activity and stability, supported Ni-catalysts are the most widely applied reforming catalysts [2,7–9]. It is rather difficult to maintain the activity of the catalyst, because tar compounds in the bio-oil can give rise to extensive coke deposition on the catalyst surface and, consequently, bring about quick catalyst deactivation [2,4,5,9,11–13]. In order to mitigate the deactivation problem, several strategies were followed, e.g., the use of less active but cheap catalytic material, such as dolomite, calcite or olivine, that can be often replaced by fresh material without considerable expense [15,19], modification of the catalyst, which is usually Ni-based, and optimization of the reaction conditions to suppress coke formation [4,8,11], development and application of quick and effective method for periodic restoration of the catalytic activity [12], or application a combination of some of the above methods. The most promising approach uses a dual catalytic system, in which a cheap, so-called guard catalyst, e.g., calcined dolomite is applied in front of an active Ni-catalyst in order protect latter catalyst from extensive contact with tar and, thereby, reduce catalyst coking and maintain its high activity for a long period of time [2,13,14,16,20].

Beside the abundantly available lignocellulosic waste materials, the animal by-products, such as meat and bone meal (MBM) represent significant biomass resource. The living animal slaughtering for meat production amounts about 42 million tons/year in the EU 27 countries http://epp.eurostat.ec.europa.eu/portal/page/portal/agriculture/data/main_tables, from which approximately 20 million tons/year animal by-products should be formed. Since MBM is considered specific risk material (SRM) which could be responsible for Bovine Spongiform Encephalopathy (BSE), its use as animal food is forbidden [21–24]. It is mandatory to treat MBM prior to disposal. Co-combustion with coal or the incineration for energetic use are the most often applied costly but biologically safe options of MBM handling [22–24]. However, environmental effect of these disposal technologies is controversial. The combustion technologies emit fly ash and other dangerous contaminants, such as furans, dioxins, and significant amount of NO_x due to the high nitrogen content (5–10 wt%) of the MBM.

The present paper relates to the thermochemical and catalytic conversion of animal by-products, particularly, to the catalytic steam reforming of pyro-oil, obtained from the pyrolysis of MBM. During pyrolysis of MBM smaller amount of malign compounds are emitted than during gasification and direct combustion

[21–24]. The process gives a carbonaceous solid (bone char, 35–40 wt%) and a gaseous stream (60–65 wt%) containing 70–80 wt% condensable fraction, the so-called bone-oil [21,22]. Most of the malign pyrolysis products remain in the pyro-oil. Former studies focused on the characterization of the pyrolysis products, especially the bio-oil, in order to establish their further application or processing.

The direct use of bone-oil as conventional fuel or fuel additive can be ruled out for the reasons mentioned above. The refining of MBM pyro-oil, according to our best knowledge, has never been attempted. The present study focuses on the development of a dual catalyst system (two different catalysts each in a separate reactor) and catalytic process for the steam reforming of the oil obtained from the pyrolysis of MBM. Two reactors were operated in cascade. The first reactor contained calcined dolomite guard catalyst, whereas the activity of different Ni/γ-Al₂O₃ catalyst preparations was tested in the second reactor. The efficiency of the guard catalyst and the effects of steam reforming conditions on the conversion and selectivity were investigated. Catalysts were prepared in particulate form or supported on cordierite monolith carrier in order to take advantage of the low flow resistance of the monolith structure under high flow conditions [25–27].

2. Materials and methods

2.1. Feedstock

Pyrolysis oil was obtained as from pyrolysis of MBM (Terra Humana Ltd., Hungary). The MBM was treated in virtual absence of oxygen using a specially designed rotary kiln at about 50 Pa below atmospheric pressure and 450–500 °C <http://www.3ragrocarbon.com>. Upon cooling the obtained pyrogas below about 350 °C a significant fraction of the gas condensed giving the bone oil, a homogeneous dark brown organic liquid of unpleasant odor. The composition and some properties of the pyrogas and the oil fraction are given in Table 1. The oil composition (C_{1.0}H_{1.95}N_{0.1}O_{0.1}) is similar to the bone-oil compositions reported by earlier studies [21,23]. Its characteristic property is the relatively high concentration of organic nitrogen. It is to be noted that the pyrolysis oil contains 5.9 wt% moisture (determined by Karl–Fisher titration) that amounts to more than half of the total oxygen content of the oil.

Table 1
Physicochemical properties of the pyrolysis gas and oil obtained from the pyrolysis of MBM.

Pyrogas		Pyro-oil ^a	
<i>Composition (wt%)</i>			
Organic compounds	45–55	C	70.0
N ₂	18–25	H	11.3
O ₂	<1	N	8.4
CO	5–12	O	10.3 ^b
CO ₂	4–8	S	–
H ₂	1–3		
Water	15–18		5.9
<i>Other properties</i>			
Higher calorific value	16 ^c MJ/m ³		36.5 MJ/kg
Residue of combustion (wt%)	–		0.09
Kinematic viscosity, cSt	–		33.38 ^d
Closed-cup flash-point (°C)	–		38 ^e
pH	–		~10
Density (kg/dm ³)	–		0.9749

^a The fraction of the pyrogas condensed at room temperature.

^b Includes the H₂O oxygen.

^c At gas temperature 450 °C.

^d At 40 °C.

^e Determined by the Pensky–Martens method.

2.2. Catalyst preparation

Dolomite was used as a guard catalyst in front of a more active Ni-catalyst. Dolomite rock (Márkakő, Ltd., Piliscsaba, Hungary) was crushed and sieved and the 0.5–1.0 mm fraction was loaded in the reactor.

Ni-catalysts were prepared in particulate form using granular γ - Al_2O_3 or alumina-coated cordierite monolith as support.

Granular γ - Al_2O_3 (Ketjen, CK-300, particle size 0.25–0.5 mm, specific surface area $195 \text{ m}^2 \text{ g}^{-1}$) was impregnated with calculated amount of a 30 wt% solution of nickel acetate. The impregnated support was calcined at 600°C for 3 h. This treatment converted the nickel acetate to NiO. Alkaline earth (Ca, Mg) and alkali metal (K) promoted particulate Ni-catalysts were also prepared. The γ - Al_2O_3 support was first impregnated by a calculated amount of a 1 M solution of Ca-, Mg-, or K-nitrate then calcined at 600°C for 3 h. The modified support was used then to prepare Ni-catalyst as described above.

Commercial cordierite monolith block of honeycomb structure (Pinxiang Zhong Tian Chemicals, China) containing 300 parallel channels per square inch was used to prepare the monolith Ni catalyst. From the block, being too large for laboratory experiments, cylindrical pieces of 0.9-cm diameter and 5-cm length were cut. As a first step the cut-out monolith piece was washcoated with γ - Al_2O_3 following the procedure given in the corresponding literature [27]. Shortly, the γ - Al_2O_3 , used also as support of the particulate Ni-catalyst, was milled to get a powder of particles smaller than about $3 \mu\text{m}$. The micronized powder was applied as a suspension containing 25 wt% of alumina in dilute nitric acid solution ($\text{HNO}_3/\text{Al}_2\text{O}_3 = 2 \text{ mmol g}^{-1}$). The monolith piece was immersed into the suspension for 1 min. After taking out the monolith piece from the suspension the channels were blown through by compressed air. This way the suspension was removed from the channels except a layer that remained adhered on the channel walls. The monolith piece was dried then at 100°C and its weight gain was measured. The same procedure was repeated until the desired weight gain (8–15 wt%) was attained. Then the alumina coated monolith piece was heated up at a rate of 1°C min^{-1} to 600°C and kept at this temperature for 10 h. This thermal treatment fixed a γ - Al_2O_3 washcoat layer on the channel walls. In order to get K, Ca or Mg promoted catalyst the washcoated monolith piece, pre-dried at 120°C , was dipped into a diluted solution of the nitrate salt of the respective metal then it was dried and calcined at 600°C for 3 h. Finally, the pre-dried monolith was dipped into a nickel acetate solution then dried and calcined again as before. The designation and the composition of the studied Ni-catalyst preparations are given in Table 2. The composition of the catalysts was calculated from the used amounts of ingredients. The amounts of ingredients used for the preparation of the monolith catalysts was determined by mass measurements. The mass difference of the cordierite and the cordierite with the alumina washcoat gave the alumina content. The average thickness of the alumina layer was calculated from the geometric surface area and the alumina

content of the monolith assuming 70% porosity for the layer. These values were 21 and $37 \mu\text{m}$ for the catalysts containing 7.1 and 12.4 wt% alumina, respectively, which correspond well with those observed on the scanning electron microscopic (SEM) images of the samples. The SEM examination suggested that the thickness of Ni/ γ - Al_2O_3 catalyst layer formed on the channel walls was 20–40 μm (vide infra). The contents of metals were calculated from the amounts and the concentrations of solutions taken up by the washcoated monolith after pre-drying.

2.3. Steam reforming

Two fixed-bed flow-through tube reactors were arranged in cascade, as shown in Fig. 1. The catalytic system comprises two identical stainless steel reactors (length = 300 mm, ID = 9 mm) in electric tube furnaces. Five grams of guard catalyst dolomite was loaded in the first reactor (bed length: $\sim 5 \text{ cm}$), whereas active Ni-based catalyst was filled into the second reactor. If particulate Ni-catalyst was used, 0.5 g of catalyst was diluted with inert α - Al_2O_3 to get an about 5-cm long catalyst bed. Both catalyst bed was placed between beds of inert 1–2 mm size silicon carbide beads in the middle of the about 10-cm long isothermal zone in the reactor tubes. In some experiments, no dolomite guard catalyst was applied. In these experiments, the Ni-catalyst was placed into the first reactor and the second reactor, not to be empty, was loaded with catalytically inert silicon carbide beads only.

Before steam reforming experiments the dolomite was calcined in situ in the reactor applying a $100 \text{ cm}^3 \text{ min}^{-1}$ air flow at 850°C for 3 h then the reactor was purged with nitrogen at the same temperature for 15 min. The Ni-catalyst was reduced in situ in a hydrogen flow at 500°C maintaining all the other condition the same as at the dolomite treatment. The reduced catalyst was heated up to the 700 – 800°C reaction temperature in the nitrogen flow. As a result of the pre-treatment, dolomite was converted to CaO-MgO mixed oxide, whereas the NiO in the Ni-catalyst was reduced to metallic nickel particles. The particle size of the nickel, determined by XRD using the Scherrer method, was 6–8 nm. When dolomite was used as guard catalyst bed in front of a Ni catalyst, the reduction of this latter catalyst was carried out first in hydrogen, then the dolomite bed was calcined in N_2 flow as described above.

The steam reforming reaction was initiated by setting the rate of the N_2 flow in the range of 15 – $28 \text{ cm}^3 \text{ min}^{-1}$ to match the estimated volume of the pyrogas, obtained from the fed-in pyro-oil (2.0 – 4.0 g h^{-1}) when gasified in the reactor. The feed rate of water (13.7 – 27.4 g h^{-1}) was adjusted to the carbon content and the feed rate of the oil to get steam to carbon molar ratio (S/C) of 5. The temperature of the top zone ($\sim 10 \text{ cm}$) in the first reactor was controlled separately and was kept at 600°C in order to provide an evaporating/mixing zone for the reactants before reaching the catalyst bed. The product mixture leaving the first reactor was fed via a heat insulated transfer line into the second reactor containing the active Ni-catalyst. The reaction products from the second reactor were passed through condensers. The condensed liquid, mostly the excess water and some unconverted oil, was collected in a liquid receiver. The separated gas was passed through a dry ice trap in order to minimize its residual water vapor content. Finally, the gas product passed through a sampling valve and was analyzed by GC. The flow rate of the effluent gas was measured by a mass flow meter equipped with a totalizing unit. This latter allowed the accurate measurement of the gas production during long experiments. (The intermittently measured effluent rate multiplied by the time of the experiment gives the amount of gas less accurately because of eventual minor fluctuations in the flow rate.) The average hourly gas production was used for further calculations.

Table 2
Composition of the catalyst preparations.

Catalyst	Concentration (wt%)				
	γ - Al_2O_3	Ca	Mg	K	Ni
Ni/ γ - Al_2O_3	80	–	–	–	20
Ni/Ca/ γ - Al_2O_3	79	1	–	–	20
Ni/Mg/ γ - Al_2O_3	79	–	1	–	20
Ni/K/ γ - Al_2O_3^a	79	–	–	1	20
M-1 ^b	7.1	–	–	0.07	1.8
M-2 ^b	12.4	–	–	0.12	3.3

^a The specific surface area of the pre-reduced catalyst was $159 \text{ m}^2/\text{g}$.

^b Monolith sample; the balance is the cordierite support.

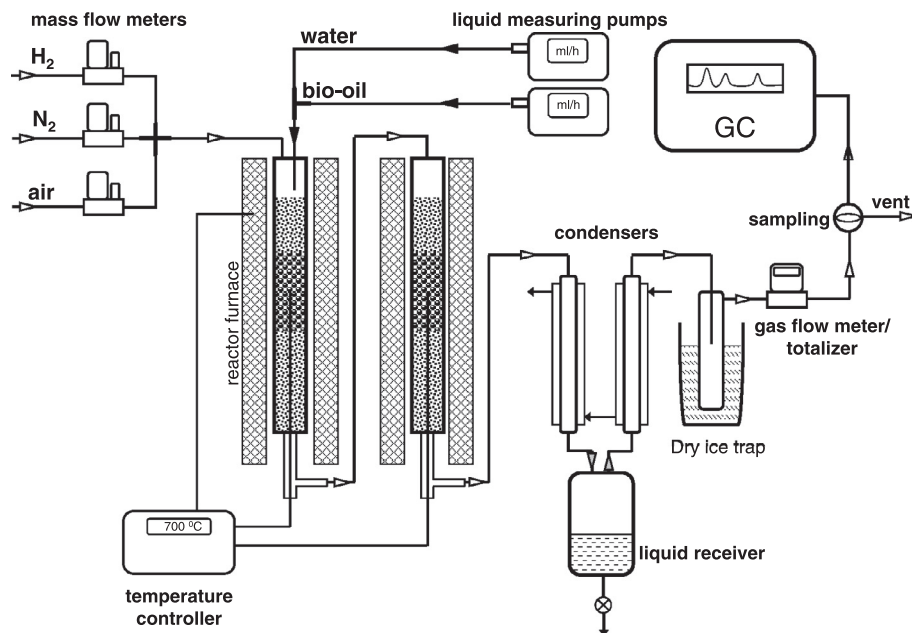


Fig. 1. Scheme of two-bed cascade catalytic reactor system for steam reforming of bone oil.

It should be mentioned that the reproducibility of the catalytic measurements was confirmed by repeating several catalytic runs at least twice. The deviation of the data obtained in these consecutive runs including conversion values and product yields was always within 5%.

2.4. Gas analysis and data treatment

The gas analysis was carried out using a gas chromatograph (GC; ChromPack 437A) equipped with a 60/80 Carboxen™ 1000 column and thermal conductivity detector (TCD). A standard gas mixture containing the component gases of the product (H_2 , N_2 , CO , CH_4 , CO_2) was used for calibration. The GC analysis gave the molar (volumetric) concentration of each component (y_i) leaving the reactor. The flow rate of component i (F_i) was calculated by the following equation:

$$F_i = \frac{F_T \cdot y_i}{100} \quad (1)$$

where F_T stands for the measured total flow rate.

The carbon conversion (X_C) was calculated by relating the molar flow rates of carbon-containing gaseous products (F_{CO} , F_{CO_2} , F_{CH_4}) to the molar feed rate of carbon in reactant oil (F_C) as given by Eq. (2) [11,13,15].

$$X_C(\%) = \frac{F_{CO} + F_{CO_2} + F_{CH_4}}{F_C} \cdot 100 \quad (2)$$

Note that the X_C gives the fraction of oil carbon converted to carbon-containing gas products. The real conversion is somewhat higher because some carbon-containing species formed from the oil feed remain deposited within the reactor.

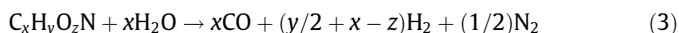
3. Results and discussion

3.1. Reactions of bone-oil steam reforming

The catalytic steam reforming of hydrocarbons and oxygen containing organic compounds, being prevailing components of bio-oils from plant origin, were extensively studied. The process is considered to involve a complex reaction network comprising multiple pathways for feedstock conversion and for secondary

reactions between the primary products [7]. The reaction mechanisms over alumina supported metal, mainly nickel, was assumed to be similar for the most different reactants [1,5,6]. The organic reactants were suggested to adsorb on the metal. Hydrogen is produced via dehydrogenation of the adsorbed molecules. The water was assumed to become activated on the surface of the alumina support. Hydroxyl groups and hydrogen atoms are obtained that are believed to migrate on the support to the metal/support interface, where they react with the metal-bound carbon-containing species generating hydrogen and carbon oxides.

The present study showed the formation of H_2 , CO , CO_2 , N_2 and small amount of CH_4 during the steam reforming of the bone-oil. Other gases, such as nitrogen oxides or higher hydrocarbons, could not be detected. These results suggest that the organic nitrogen and oxygen in the bone-oil was converted to molecular nitrogen and water, respectively. The gross steam reforming reaction can be given by the following equation:



The hypothetical reactant molecule, calculated from the pyro-oil composition of Table 2, by assuming that, like most of the simple amino acids, each molecule contains one nitrogen atom, is $C_{8.97}H_{17.29}O_{0.78}N$. The molecular mass of this molecule is 151.5. That suggests that the compounds of the pyro-oil contain as an average about nine $-CH_2-$ units.

Because steam is used in excess required by the above stoichiometry, the reaction is accompanied by water gas shift (WGS) reaction between the reforming product carbon monoxide and the available water (Eq. (4)) [5,6], resulting in the appearance of CO_2 as product.



Beside the above mentioned main processes, different side reactions take place. Small amount of methane was formed by the methanation of carbon oxides or more probably by hydrocarbon hydrogenolysis. The exothermic methanation, as expected, is suppressed at higher temperatures as it was observed and reported recently [7,28]. The product distribution is controlled by the thermodynamics. It changes as the equilibrium of the reactions shifts with the reaction conditions.

Activity decay was experienced due to catalyst coking. The possible reasons of coking were revealed by previous studies. Higher unsaturation of the reactant compounds was shown to lead to stronger coke formation. Also, the components of high aromaticity and molecular weight, the so called tar compounds, readily form deposit on the catalyst leading to activity loss and, in extreme cases, reactor plugging [5,11]. The presence of tar compounds in the reactant explains the need for use of guard catalyst in the catalytic bone-oil steam reforming process.

3.2. Calcined dolomite as guard catalyst

The catalyst deactivation during steam reforming is generally attributed to extensive catalyst coking, which seems to be unavoidable due to the tar content of most pyro-oils [12,13]. Catalyst lifetime has an utmost importance in the steam-reforming practice. The catalyst deactivation is slower if the reaction between the steam and the carbonaceous surface species is faster. Thus, an obvious strategy of slowing deactivation is to use of steam in large excess to oil (high S/C ratio) and to increase the reaction temperature [2,7,17]. It should be noted that the application of increased S/C ratios and/or temperatures decreases the economy of the steam reforming process and the somewhat slower activity decay does not really solve the problem. A solution alternative was the effective continuous or frequent catalyst regeneration. In order to regenerate the catalyst of a flow-through fixed bed reactor, as the one used in this study, the reaction has to be interrupted and the catalyst has to be contacted with fluid that removes the deposited coke.

The Ni/ γ -Al₂O₃ catalyst, when used alone for bone-oil steam reforming, suffered quick deactivation (Fig. 2). The deposited coke was visible on the used catalyst particles taken from the reactor. In this work, the treatment at high-temperature with steam or air was tested as method for restoring or maintaining catalyst activity. The activity of the deactivated Ni-catalyst could not be fully restored by either of the treatments and tended to become lower as the reaction-regeneration cycles were repeated (not shown). Therefore, other solutions were needed to circumvent the problem associated with catalyst deactivation. The option of using a cheap guard catalyst, such as dolomite, having a considerable reforming activity and good tar retention was studied. The guard catalyst

permitted long and uninterrupted use of the Ni-catalyst. Regeneration the dolomite guard catalyst or its replacement for fresh catalyst was necessary only when the increased pressure drop on the dolomite bed indicated significant tar deposition in the reactor (vide infra). The dolomite guard catalyst could be regenerated many times applying steam at the temperature of the reforming reaction. The regeneration was more effective, if steam was replaced by air flow, and thereby reducing the regeneration time (not shown).

The calcined dolomite guard catalyst itself has considerable activity in the bone-oil conversion (Fig. 2b1, b2), whereas the product distribution was practically the same as over the Ni catalysts (not shown). Under the applied reaction conditions, comparable initial conversion values were obtained than over the Ni-catalyst (Fig. 2). Note however, that at least ten times more dolomite catalyst was applied than Ni-catalyst that implies a ten times smaller WHSV in the dolomite reactor. At so low reactant load the calcined dolomite, as catalyst, did not show any deactivation for several hours on stream, whereas the Ni-catalyst, being on stream for the same period of time, lost about 80% of its initial bone-oil conversion activity (Fig. 2a). These results strongly suggest that calcined dolomite could be used as a cheap and easy-to-regenerate guard catalyst in front of more active Ni catalysts (vide infra).

3.3. Guard catalyst/Ni-catalysts system

Results of bone-oil steam reforming over dual catalyst system, set in cascade of two catalyst beds are shown in Fig. 3. The reaction mixture passed first through a bed of calcined dolomite and then a bed of particulate Ni-catalyst. Stable and high conversion (>90%) was obtained. When the support was modified with potassium or calcium (Ni/K/ γ -Al₂O₃ and Ni/Ca/ γ -Al₂O₃) the catalytic properties considerably improved relatively to the Ni catalyst supported on the parent γ -Al₂O₃ (Ni/ γ -Al₂O₃), whereas modification with magnesium (Ni/Mg/ γ -Al₂O₃) had an adverse effect. Especially good results were obtained on the potassium modified sample, which showed high activity (>99% conversion) and stability during the catalytic test (>24 h). The product distribution, which was very similar for all the studied catalysts, is shown for this latter catalyst in Table 3. The product gas mixture contained 56–60% H₂, 5–6% CO, 17–20% CO₂, 3–5% CH₄, and 13–25% N₂. Note that the N₂ in the product mixtures involves the nitrogen carrier gas and N₂ formed in the steam reforming reaction (Eq. (3)).

Although the effects of alkaline and alkaline earth metal modifiers are not fully understood yet, it is generally accepted that these

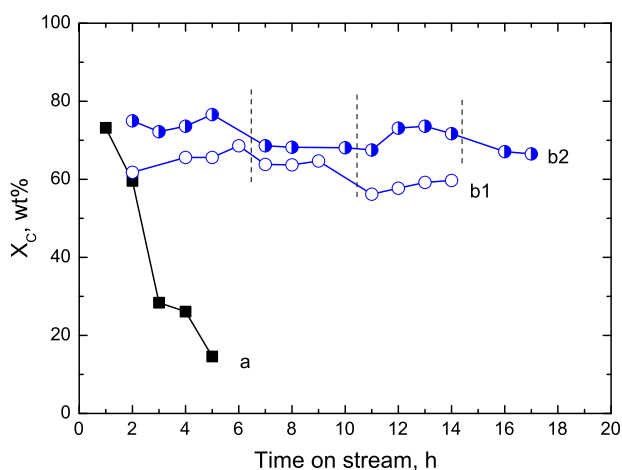


Fig. 2. Carbon conversion (X_c) as function of time on stream during catalytic steam reforming of bone oil at steam to carbon molar ratio of 5 at 800 °C over (a) 20%Ni/ γ -Al₂O₃ at WHSV = 8 g_{oil} g_{cat}⁻¹ h⁻¹ and (b1, b2) calcined dolomite catalyst at WHSV = 0.8 and 0.4 g_{oil} g_{cat}⁻¹ h⁻¹, respectively. Vertical dashed lines indicate that experiment was interrupted. Before it was continued the dolomite catalyst was treated first with pure steam at 800 °C for 30 min.

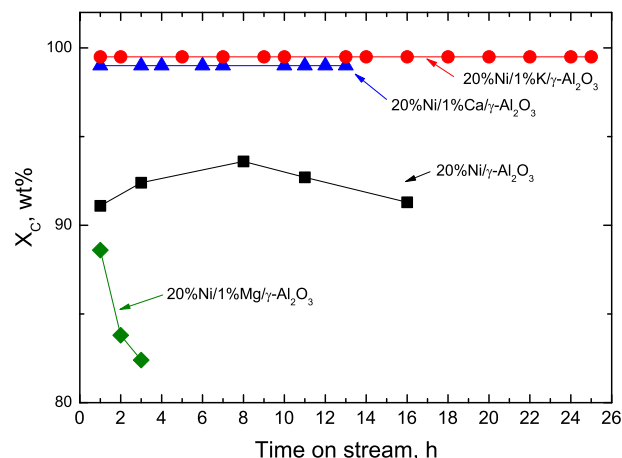


Fig. 3. Carbon conversion (X_c) as function of time on stream during catalytic steam reforming of bone oil over dual catalytic cascade reactor system consisting calcined dolomite guard catalyst (800 °C, WHSV = 0.4 g_{oil} g_{cat}⁻¹ h⁻¹) and Ni-catalyst (750 °C, WHSV = 4 g_{oil} g_{cat}⁻¹ h⁻¹).

Table 3

Product distribution of bone-oil steam reforming over alumina supported Ni catalysts.

Catalyst	T ^a (°C)	WHSV ^b (h ⁻¹)	S/C ^c	TOS ^d (h)	H ₂ mol% (L h ⁻¹) ^f	N ₂ ^e	CO	CH ₄	CO ₂	X _C ^g (wt%)
Ni/K/ γ -Al ₂ O ₃ ^h	750	8 (0.8)	5	7	58.3 (8.96)	13.2 (2.05)	5.0 (0.78)	3.8 (0.77)	19.7 (3.95)	97.9
	750	4 (0.4)	5	35	56.2 (4.85)	14.6 (1.27)	6.3 (0.55)	5.2 (0.59)	17.7 (2.00)	>99
M-1 ^h	750	18 (0.8)	5	13	58.9 (9.05)	13.6 (2.11)	5.8 (0.90)	4.2 (0.86)	17.5 (3.51)	94.0
	750	9 (0.4)	5	19	56.6 (4.89)	16.0 (1.39)	5.3 (0.47)	4.3 (0.49)	17.8 (2.00)	>99
	700	9 (0.4)	5	24	56.4 (4.65)	14.3 (1.19)	5.2 (0.43)	4.6 (0.50)	19.5 (2.09)	>99
M-2 ^h	700	9 (0.8)	5	11	59.8 (9.37)	11.3 (1.79)	4.9 (0.78)	4.6 (0.94)	19.4 (3.74)	>99
	700	4.5 (0.4)	5	16	59.0 (5.33)	11.6 (1.06)	9.6 (0.87)	4.6 (0.55)	15.2 (1.79)	>99
M-2 ⁱ	700	9 (0.8)	5	12	60.3 (10.3)	11.4 (1.98)	5.0 (0.87)	4.1 (0.93)	19.2 (4.31)	>99
	700	4.5 (0.4)	5	18	58.4 (4.86)	12.9 (1.08)	5.7 (0.48)	4.4 (0.49)	18.6 (2.03)	>99
	700	4.5 (0.4)	3	23	58.1 (5.24)	11.9 (1.08)	8.4 (0.77)	4.1 (0.49)	17.5 (2.06)	>99

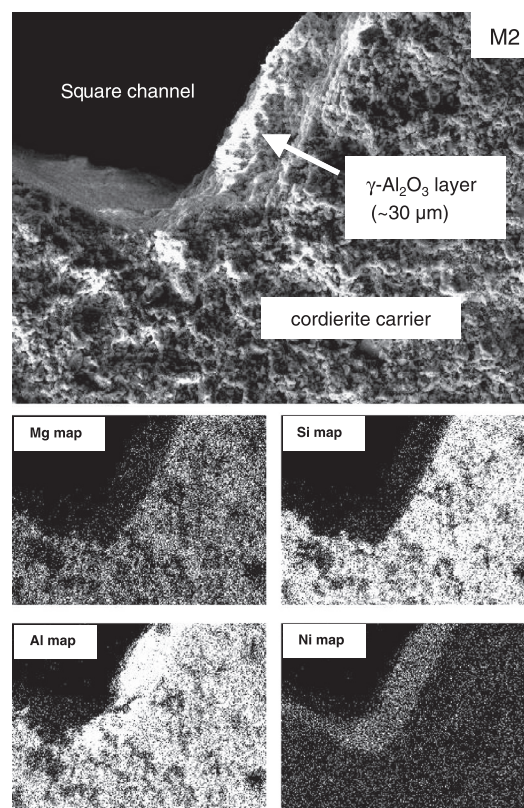
^a Reaction temperature (the dolomite guard bed was kept always at 800 °C).^b Weight hourly space velocity based on the weight of the Ni-catalyst, not including the weight of the cordierite support (the values in parenthesis are the WHSV for the dolomite guard bed).^c Steam to carbon molar ratio of the feed.^d Time on stream.^e Nitrogen carrier gas and N₂ produced in the steam reforming reaction.^f Molar composition of the non-condensable reactor effluent (values in parenthesis: the flow rates of component gases produced).^g Carbon conversion.^h Catalyst was pre-reduced in H₂ at 500 °C. The specific surface area of the fresh, pre-reduced catalyst was 159 m²/g, whereas that of the used catalyst was 118 m²/g.ⁱ The catalyst was used without pre-reduction.

modifiers can stabilize the γ -Al₂O₃ support against sintering, decrease its acidity and thereby suppress the cracking and polymerization reactions leading to coke deposition, and most importantly can enhance steam adsorption on the support [2,8,11,14,16]. The enhanced steam adsorption accelerate the gasification of organic fragments and coke deposits on the catalyst surface. In the present study, modification of the γ -Al₂O₃ support with Ca or K resulted in a significant promotional effect as reflected by the stable and nearly 100% conversion values (Fig. 3). The adverse effect of Mg modification is presently not understood and further investigations are needed to clarify this point.

3.4. Monolith catalysts

The high temperature and the increasing number of molecules in the reactor (Eq. (3)) bring about an enormous sudden increase of the gas volume and linear gas velocity that can be as high as several 100 m/s. To reduce the pressure drop on the catalyst bed at high flow conditions the active catalyst is preferably formulated to have low resistance to flow. In the present study steam reforming experiments were carried out with catalyst supported on cordierite monolith carrier. Honeycomb monolith catalysts had already been used in various gas phase catalytic reactions [25], even in steam reforming [26,27], but were not tested before in the steam reforming of bone oil.

An uniform layer of active Ni catalyst was formed on the surface of cordierite monolith support. The composition of the thus obtained catalyst layer was nearly the same as that of the particulate Ni catalyst (Table 2). The thickness and uniformity of the catalyst layer and the distribution of the active Ni component was checked by scanning electron microscopy (SEM). The SEM image of the cross section of monolith catalyst M2 (top view) together with the corresponding Mg-, Si-, Al-, and Ni-maps are shown in Fig. 4. The ~30 μ m thick γ -Al₂O₃ layer can be clearly distinguished from the macroporous wall of the cordierite support (Fig. 4, top). The Mg- and Si-maps are fully overlapping, since these elements can be found only in the material of cordierite (composition: 2MgO:5SiO₂:2Al₂O₃ [27]). As shown on the Al-map, the concentration of Al in the γ -Al₂O₃ layer is necessarily higher than in the cordierite support (the density of white dots is proportional with the concentration of the respective element). The Ni-map clearly

**Fig. 4.** SEM characterization of the M2 monolith catalyst.

shows that Ni introduced by impregnation is mostly located in the γ -Al₂O₃ layer, and therefore it must be readily accessible for the reactant molecules.

The catalytic properties of the monolith catalysts and the corresponding particulate Ni/K/ γ -Al₂O₃ catalyst are compared in Table 3. Results show that under the same reaction conditions, the same high conversion (>99%) and very similar product distribution can be achieved on both types of catalyst. Therefore, we can conclude that the particulate catalyst can be easily replaced by monolith catalysts, which are expected to provide significantly lower flow

resistance in the catalyst bed [26]. Results also show that the pre-reduction of the Ni catalyst can be omitted, since the catalyst is quickly reduced most probably by H_2 and CO formed on the calcined dolomite guard catalyst at the beginning of the steam reforming reaction (Table 3, last row).

3.5. Energy balance considerations

It is difficult to calculate exact energy balance for the steam reforming of a real pyro-oil even if 100% conversion to gas is assumed because of the hundreds of compounds present in the oil and the several parallel and consecutive reactions that control the composition of the product gas. For simplicity we do not consider the hard-to-calculate energy losses of a real steam reforming process and to further simplify the calculation we deal with for the steam reforming of the $-CH_2-$ hydrocarbon moieties of the reactant.

The energy input of the process is the chemical energy of the pyro-oil and the heat demand of the endothermic reaction, whereas the output of the process is the chemical energy of the reactor effluent. It follows from the energy conservation rule that the chemical energy of the effluent must be equal with the sum of the chemical energy of the reactant and the energy introduced into the reaction. Latter is the heat demand of water evaporation and steam overheating to the temperature of the reaction plus the heat of reaction endothermicity. The ratio of the combustion heat (ΔH_{com}) of the product gas to the required heat input is the energy efficiency of the conversion of one energy carrier (pyro-oil) into another energy carrier (synthesis gas).

For the stoichiometric steam reforming of a $-CH_2-$ moiety ($-CH_2- + H_2O \rightarrow CO + 2H_2$), where $S/C = 1$, the combustion heat of the product gas is

$$\Delta H_{com} = LHV_{CO} + 2 \times LHV_{H_2} = 283.24 + 488 = 771.24 \text{ kJ},$$

where LHV stands for the molar lower heating value at 15.4 °C.

The required energy input (ΔH_{in}) was estimated as

$$\begin{aligned} \Delta H_{in} &= L_{evap.} + c_{p,steam} \Delta T + \Delta H_{react.} = 40.9 + 25.2 + 163.24 \\ &= 229.34 \text{ kJ/mol}, \end{aligned}$$

where $L_{evap.}$ means the molar evaporation heat of water, $c_{p,steam} \Delta T$ is the energy demand of steam overheating to 800 °C, and $\Delta H_{react.}$ stands for the endothermicity of the reaction. (The reactant was assumed to be gas. In the calculation the enthalpy change of the reactant and product gases between the reference temperature (15.4 °C) and reaction temperature was neglected.) The $\Delta H_{com}/\Delta H_{in}$ ratio is 3.5. In other words, total energy output of the conversion process $[(\Delta H_{com} + \Delta H_{in})/\Delta H_{com}] \times 100\%$ is about 130%, the net energy gain of the process $[(\Delta H_{com} - \Delta H_{in})/\Delta H_{com}] \times 100\%$ is about 70%, relative to the chemical energy of the reactant.

The C/N ratio of the steam-reformed pyro-oil was about 9. In order to learn about the effect of heteroatom in the molecules of the oil on the energy efficiency of the reforming process calculations, similar to that above, were made for nonane (C_9H_{20} , LHV = 5729.0 kJ/mol [29]) nonyl alcohol ($C_9H_{20}O$, LHV = 5779.0 kJ/mol [30]), and nonylamine ($C_9H_{21}N$, LHV = 6340.3 kJ/mol [31]). In reaction with 9 mol H_2O 1 mol reactant gives 9 mol CO. The amount of H_2 , used in the calculation, was the smallest for the alcohol (18 mol), the highest for the amine (19.5 mol) and was in-between of these two for the nonane (19 mol). The endothermicities of reforming C_9 amine, alcohol, and alkane are 966.7, 1162.2, and 1456.2 kJ/mol, whereas the corresponding $\Delta H_{com}/\Delta H_{in}$ energy efficiency values are 4.68, 3.95 and 3.50, respectively. It can be concluded that the presence of alcohol or amine group substituent on an alkane increases the combustion heat of the molecule relative to that of the alkane, decreases the endothermicity of the reforming

reaction and improves the efficiency of the energy conversion process.

The difficulty of realizing efficient catalytic steam reforming relies in the need for using water in excess to stoichiometric amount to avoid excessive catalyst coking and deactivation. The above outlined energy benefit can be obtained only if all the enthalpy of the excess overheated steam can be recovered. The process according to the above model becomes energy neutral if the S/C molar ratio is raised from 1 to 9.2 and the steam energy is not recuperated. In this case, the CO/ H_2 product mixture carries as much chemical energy as was used to convert the reactant to the product gas. In such a case the only benefit of the process, combining pyrolysis and steam reforming, is that it provides an environmentally friendly way for neutralizing dangerous organic wastes, such as animal by-products.

4. Conclusions

A large fraction of MBM can be converted into easy-to-transport, non-infectious, high energy density bio-oil by pyrolysis. Because the oil is toxic and carcinogen the pyrolysis transforms a biohazard to a chemical hazard. Steam reforming of the oil, using a two-bed cascade reactor, comprising of a calcined dolomite guard catalyst and an active supported Ni-catalyst, provides solution for this problem. The oil can be virtually fully converted into gas, rich in CO and H_2 . Thereafter the gas can be used directly to fuel internal combustion gas engine or, after purification, as syngas for producing liquid motor fuel by Fischer–Tropsch technology.

Acknowledgements

This work was supported by the National Development Agency (Project No. GOP-1.1.1.-08/1-2008-0010), the European Union and co-financed by the European Social Fund in the frame of the TAMOP-4.2.1/B-09/1/KONV-2010-0003 and TAMOP-4.2.2/B-10/1-2010-0025 projects.

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